JOURNAL OF CHEMICAL & ENGINEERING DATA

COMMENT/REPLY

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Comment on "Thermodynamics of Solvent Extraction of Rhenium with Trioctyl Amine" (Fang, D.-w.; Gu, X.-j.; Xiong, Y.; Yue, S.; Li, J.; Zang. S.-l. *J. Chem. Eng. Data* 2010, *55*, 424−427) and "Studies on Solvent Extraction of Perrhenate with Trialkylamine by Debye−Hückel and Pitzer Equations" (Fang, D.-w.; Gu, X.-j.; Xiong, Y.; Shan, W.-j.; Zang, S.-l. *J. Chem. Eng. Data* 2010, *55*, 4440−4443)

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ABSTRACT: Some concerns are raised regarding the value of the tabulated Pitzer activity coefficient model parameters for NH_4ReO_4 presented in two recent papers (Fang et al., *J. Chem. Eng. Data* **2010**, *55*, 424−427 and Fang et al., *J. Chem. Eng. Data* **2010**, *55*, 4440−4443). The use of these parameter sets is not recommended, as it leads to the calculation of activity coefficients which are inconsistent with the known behavior of similar salts.

The purpose of this comment is to express some concern regarding the parametrization of the Pitzer activity coefficient model in the solvent exchange systems described in the two recent *J. Chem. Eng. Data* papers of Fang et al.[1,2] In this work, the Pitzer model has been applied to the description of the aqueous-phase interaction of ReO_4^- with NH_4^+ in an acidified NH_4Cl solution, with ion interaction and equilibrium parameters obtained by least-squares fitting of experimental concentration product data. However, both the methodology applied and the results obtained raise some significant issues which call into the question the validity of the results obtained and, thus, the value of the published Pitzer model parameter sets. Some of these concerns are detailed briefly in this comment.

The work of Fang et al.[1,2] uses the Pitzer ion interaction model[3−5] to analyze micromolar concentrations of ReO_4^- in background electrolytes of ionic strength up to 2.0 $\text{mol}\cdot\text{kg}^{-1}$. However, the first problem with the model parametrization as presented is that, instead of fitting the standard Pitzer model second virial coefficient parameter $\beta^{(1)}$—which is a constant in the standard formulation of the model—the authors have instead fitted the combination they refer to as $y_1\beta^{(1)}$, where y_1 is the ionic-strength dependent term given by eq 1:[4,6]

$$y_1(x) = \frac{2}{x^2}[1 - (1 + x)e^{-x}] \qquad x = 2\sqrt{I} \qquad (1)$$

In each of their papers, Fang et al.[1,2] treat $y_1\beta^{(1)}$ as a constant over the ionic strength range (0.1 to 2.0) $\text{mol}\cdot\text{kg}^{-1}$. This violates the convention that $\beta^{(1)}$ itself should be the constant quantity and means that the parameters fitted to this nonstandard form of the model are not able to be used in any of the many widely used software packages which apply the standard Pitzer model. There is no strong theoretical justification for the specification of $y_1\beta^{(1)}$ as a constant; although the functional form used in the standard Pitzer model was chosen empirically,[3] it has now become effectively standardized, and it appears that little is to be gained by its arbitrary modification.

The second, and probably more serious, problem is related to the numerical values of the Pitzer model parameters themselves. It should be remembered that the Pitzer model directly predicts activity and/or osmotic coefficients. Activity coefficients are fitted by Fang et al.[1,2] via their role in equilibrium calculations, rather than directly from experimental activity or osmotic coefficient data. It is therefore suggested that a useful "sanity check" on the parameter values may be obtained by directly plotting the activity coefficients obtained from the Pitzer model and comparing them against the available data for similar electrolytes. Experimental data for NH_4ReO_4 itself do not appear to be available, but it is instructive to compare the model predictions with experimental data for alkali metal perrhenates and for related ammonium salts such as NH_4ClO_4, for which data are available in the literature. A similar approach has previously been taken in the analysis of the aqueous sodium silicate system,[7] where a previously published set of parameters which had been obtained from speciation data were shown to provide spurious activity coefficients, and a new set were estimated based on available data for related oxyanions.

Figure 1 therefore presents such a comparison for the case of NH_4ReO_4, showing the Pitzer model activity coefficient predictions obtained using the parameter sets of Fang et al.,[1,2] for a temperature of 298.15 K (including the constant $y_1\beta^{(1)}$ values). Two data sets for NH_4ReO_4 are shown in Figure 1, because refs 1 and 2 each present a different set of Pitzer model parameters for NH_4ReO_4. This is problematic in itself, as these parameters (and the activity coefficients) should not be influenced strongly by a

Received: December 6, 2010
Accepted: January 5, 2011
Published: January 21, 2011

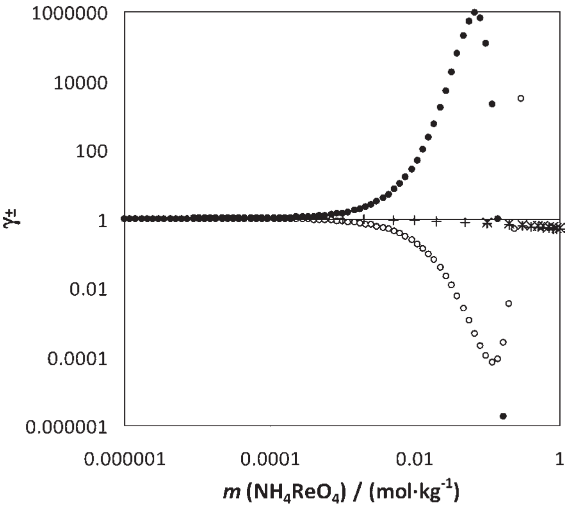

Figure 1. Activity coefficients $\gamma_\pm$ for NH_4ReO_4 at 298.15 K, calculated using the parameters of ref 1 (●) and ref 2 (○). Points are not shown beyond activity coefficient values of $10^{\pm 6}$; the activity coefficients calculated at a concentration of 0.5 mol·kg^{-1} are around 10^{-220} for the ref 1 parameter set, and 10^{34} for ref 2. For comparison, experimental activity coefficient data for $NaReO_4$ (×) (ref 8) and NH_4ClO_4 (+) (ref 9) are also shown.

change in the extractant present, due to its very low concentration in the aqueous phase. Figure 1 also shows literature data for the related salts $NaReO_4$ (from ref 8) and NH_4ClO_4 (from ref 9). It would be expected that NH_4ReO_4 should follow a similar trend, and the fact that the model predictions deviate so far from the known behavior of similar salts should immediately raise concerns.

The difference between the filled and the unfilled points in Figure 1 represents the differences in the signs of the Pitzer model parameters, specifically the second virial coefficient term $\beta^{(0)}$, given in refs 1 and 2. In ref 1, $\beta^{(0)}$ at 298.15 K is given as 202.6; in ref 2, $\beta^{(0)}$ is −72.5. The third virial coefficient C parameters also differ in sign between the two papers but have a less marked impact on the model predictions than $\beta^{(0)}$ according to a simple numerical analysis of the model equations. It should also be noted that the signs and magnitudes of the $\beta^{(0)}$ parameters obtained at 5 K temperature intervals in both refs 1 and 2 fluctuate very unpredictably as temperature increases, which raises further concerns regarding their validity.

The cause of these problems in parameter-fitting is in fact reasonably straightforward. The model was fitted to a data set using a concentration region (less than $2 \cdot 10^{-5}$ mol·kg^{-1} ReO_4) in which the sensitivity of the system to variation in the fitting parameters was very low; this can be seen in Figure 1, where the activity coefficients even at a concentration of 10^{-4} mol·kg^{-1} NH_4ReO_4 do not differ from unity by more than 3 %, and so a least-squares fit conducted with micromolar ReO_4^- concentrations (even with the relatively high concentrations of NH_4^+ and high ionic strengths present) will produce numerically spurious results. The magnitudes of the Pitzer model parameters presented in refs 1 and 2 differ from those available in the literature for similar salts (perchlorates and pertechnetates with univalent cations)[4,10,11] by factors of up to 1000; more usual $\beta^{(0)}$ and $\beta^{(1)}$ parameter values for such salts are between −0.5 and 0.5, and the magnitude of the C parameter is rarely more than 0.01 for 1:1 salts, where it is claimed to be as large as 5000 in ref 2. This can only be attributable to numerical error in the parameter fitting procedure due to the low sensitivity of the objective function (least-squares error in ReO_4^- concentrations) to variations in the parameter values.

The conclusion of this comment may then be summarized as follows: it is essential to conduct parameter fitting over a sufficiently wide concentration range, to check the obtained parameters against available sources of experimental data for related systems if direct experimental comparisons are not possible and to ensure that model equations obtained from the literature are reproduced and applied correctly. Only if these conditions are met can the parameters obtained be considered sufficiently trustworthy to be used by other investigators. The use of the parameter sets published in refs 1 and 2 is therefore not recommended.

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